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Application of Supercritical CO_2 in Enhanced Geothermal Systems: Calibration of Kinetic Rates from Batch Experiments

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- All project partners / collaborators:
  - University of Wyoming
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  - Many individuals…

Introduction

- Advantages and disadvantages of CO_2 as a working fluid in EGS reservoirs;
- Previous experimental and numerical studies on the chemical reactions with CO_2 injection in EGS reservoirs.
- The data of kinetic rates of mineral reactions are sparse and less consistent at the elevated temperature and pressure in CO_2-EGS.
- The objective of this study to calibrate and evaluate the kinetic rates of minerals from the batch experiment data.

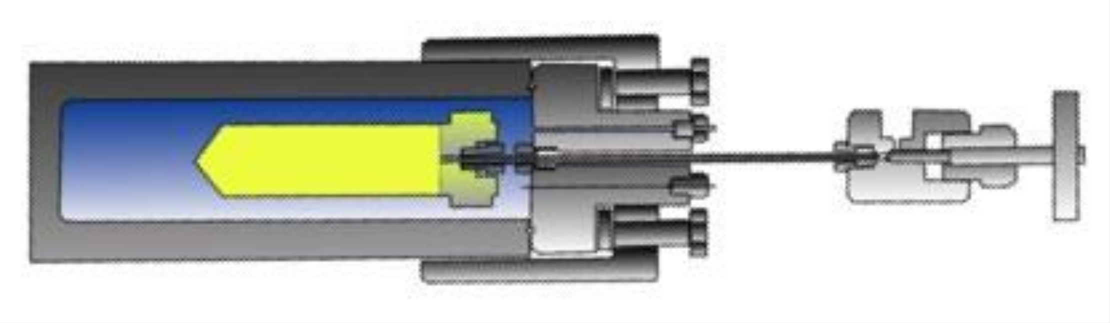
Methods and Materials

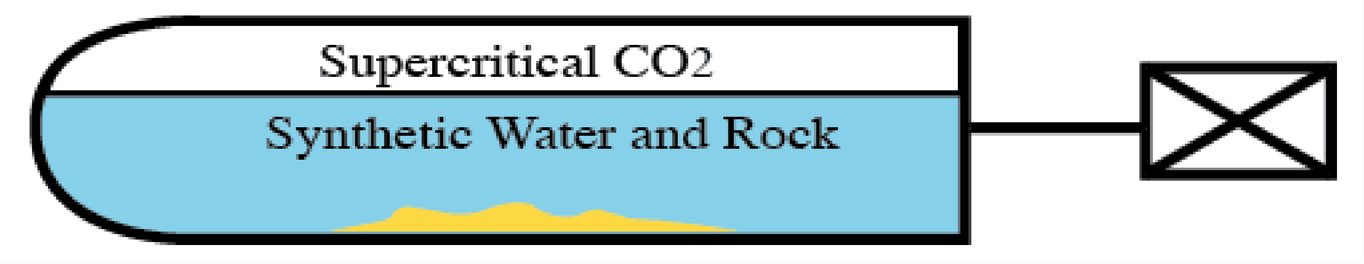
- Batch Experiments
  - Five hydrothermal fluid-rock experiments (designed to emulate the geothermal conditions)
  - Baseline water-granite experiment
  - Two water-granite-scCO_2 experiments
  - Two water-epidote-granite$\pm$scCO_2 experiments

- Numerical Tools
  - Reactive transport model: TOUGHREACT code
  - Parameter estimation tool: iTOUGH2-PEST

Experimental Apparatus

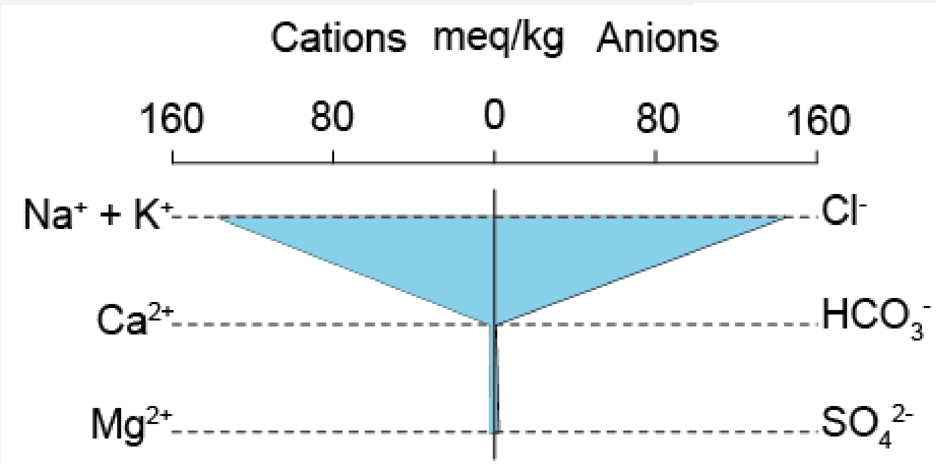
- Rocker bombs
- Flexible Au-Ti reaction cells



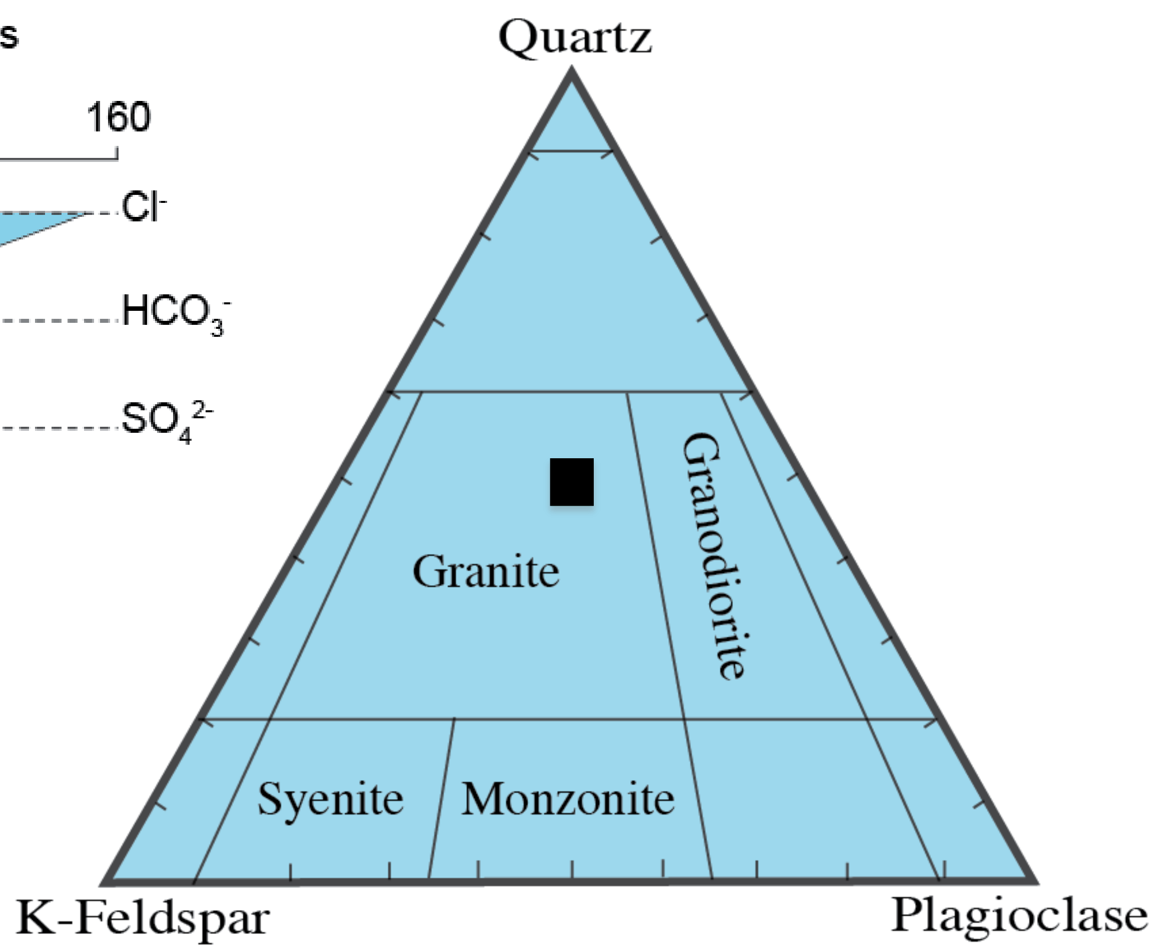


Experimental Design

- Experiments designed to emulate geothermal conditions:



- Na-Cl dominant water
  - Ionic strength ~0.1
- Granitic Mineralogy
  - Equal parts K-feldspar, plagioclase, quartz
  - 4% biotite
  - 75% powder, 25% chip



Experimental Conditions

- Experimental conditions: 250 ° C, 250-450 bars

Experiment	Water + Granite	Moderate pH Water + Granite + $scCO_2$	Low pH Water + Granite + $scCO_2$	Water + Granite + Epidote	Water + Granite + Epidote + $scCO_2$
Initial pH	5.6	5.7	3.9	5.07	5.15
Temperature ° C	250	250	250	250	250
Pressure (MPa), Pre-Injection	25.3	25.0	25.2	~24.9	~25.3
Pressure (MPa), Post-Injection	--	30.7	44.8	--	~33.8
Initial Water/Rock Ratio	19.3	20.0	19.0	20.0	20.4
Total Reaction Time (days)	42.7	72.0	74.8	35.8	54.8

Mineral components and initial surface area

Elemental Weight Percent of Mineral Reactants (Wt% oxide)					
Component[a,b]	Quartz (Qtz)	Oligoclase (Olg)	K-Feldspar (Kfs)	Biotite (Bt)	Epidote (Ep)
P_2O_5	DL	DL/NM	DL	DL/NM	DL
MnO	DL	0.01/DL	0.00	1.03/0.87	0.09
Fe_2O_3	0.08	0.12/0.04	0.19	22.84b	12.81
FeO	--	--	--	17.65c	--
MgO	DL	DL/DL	DL	13.78/13.82	DL
SiO_2	97.79	64.29/61.83	62.48	36.17/38.21	34.70
Al_2O_3	0.59	24.47/24.25	18.92	11.56/11.33	22.63
CaO	DL	5.23/4.65	0.22	0.10/0.01	23.69
TiO_2	0.03	0.02/DL	0.01	2.50/2.12	0.12
Na_2O	DL	8.36/8.67	2.35	0.60/0.43	DL
K_2O	DL	0.71/0.50	12.60	8.93/9.37	DL
F	NM	NM/DL	NM	NM/2.57	NM
Cl	NM	NM/DL	NM	NM/0.04	NM
Total	98.48	103.37/99.94	96.86	97.50/96.44	94.04
Source	Unknown	Mitchell County, North Carolina	Unknown	Ontario, Canada	Unknown
Surface Area of Unreacted Powders (m^2/g)[c]					
EXP-1	0.3367 ± 0.0028	0.6303 ± 0.0070	0.4408 ± 0.0208	1.5652 ± 0.0420	N/A
EXP-2	0.3367 ± 0.0028	0.6303 ± 0.0070	0.927 ± 0.0385	1.5652 ± 0.0420	N/A
EXP-3	0.3367 ± 0.0028	0.6303 ± 0.0070	0.4408 ± 0.0208	1.5652 ± 0.0420	N/A
EXP-4	0.7124 ± 0.0031	0.6303 ± 0.0070	0.927 ± 0.0385	1.5652 ± 0.0420	0.6327 ± 0.0617
EXP-5	0.7124 ± 0.0031	0.6303 ± 0.0070	0.927 ± 0.0385	1.5652 ± 0.0420	0.6327 ± 0.0617

From Lo Re et al. (2014)

Aqueous Geochemistry

EXP-1: Water chemistry (mmol/kg), water + granite experiment

Time (hours)	pH (STP)[a]	pH (in-situ)[b]	F	Cl	SO_4	Na	K	Ca	Mg	Fe	SiO_2(aq)	Al	Mn	ΣCO_2[f], bench	ΣCO_2[g,h], in-situ	Charge Balance[i]
Initial Water[c]	5.6 ± 0.1	6.4	0.01	161	0.81	130	8.8	1.0	0.8	<0.00002	3.4	0.0022	0.00012	0.10	*0.10*	-6.6%
25.1	5.7 ± 0.1	6.6	0.04	161	0.87	135	9.7	1.4	0.3	<0.00002	6.0	0.0063	0.00191	0.10	*0.10*	-4.5%
41.5	5.4 ± 0.1	6.6	0.05	158	0.85	129	9.4	1.5	0.2	<0.00002	6.8	0.0049	0.00080	0.34	*0.34*	-6.0%
113.5	5.6 ± 0.1	6.5	0.05	158	0.78	130	8.3	1.6	0.2	<0.00002	7.4	0.0085	0.00066	0.11	*0.11*	-5.7%
354.0	5.6 ± 0.1	6.5	0.06	157	0.75	130	9.1	1.7	0.2	<0.00002	7.6	0.0091	0.00037	0.16	*0.16*	-5.0%
640.9	5.4 ± 0.4	6.5	0.02	149	0.69	135	8.2	1.5	0.2	<0.00002	8.3	0.0061	0.00076	0.46	*0.46*	-1.5%
1023.6	5.5 ± 0.4	6.4	0.05	161	0.70	128	9.4	4.9	0.3	<0.00002	8.1	0.0066	0.00286	0.27	*0.27*	-4.7%
Quench[d]	5.1 ± 0.1	5.1	0.04	148	0.71	122	8.2	1.8	0.2	<0.00002	7.5	0.0081	0.00378	0.02	*0.02*	-5.5%
Uncertainty ± 1σ	--	--	0.02	10	0.04	4	0.4	0.3	0.1	--	0.5	0.0006	0.00007	±3.0%	--	--
Predicted Equilibrium Value[e]	--	6.2	--	142	0.64	132	10.3	0.1	0.001	0.005	6.2	0.003	--	--	0.1	--

EXP-2: Water chemistry (mmol/kg), moderate pH water + granite + $scCO_2$ experiment

Time (hours)	pH (STP)[a]	pH (in-situ)[b]	F	Cl	SO_4	Na	K	Ca	Mg	Fe	SiO_2(aq)	Al	Mn	ΣCO_2[f], bench	ΣCO_2[g,h], in-situ	Charge Balance[i]
Initial Water[c]	5.7 ± 0.1	6.4	0.01	149	0.73	123	8.9	1.4	0.7	<0.00002	3.6	0.0019	0.00013	0.10	*0.10*	-5.3%
22.6	6.0 ± 0.2	6.7	0.01	137	0.62	123	8.1	1.8	0.2	<0.00002	5.8	0.0036	0.00061	0.56	*0.56*	-1.3%
49.9	5.4 ± 0.1	6.5	0.04	140	0.67	127	10.7	2.4	0.2	<0.00002	6.7	0.0038	0.00078	0.65	*0.65*	0.5%
117.9	5.3 ± 0.1	6.5	0.04	137	0.74	132	9.4	1.6	0.1	<0.00002	7.6	0.0057	0.00079	0.49	*0.49*	2.1%
356.7	5.5 ± 0.3	6.5	0.03	136	0.53	130	8.9	1.8	0.2	<0.00002	7.7	0.0044	0.00062	0.57	*0.57*	2.2%
693.0	5.4 ± 0.1	6.5	0.02	137	0.68	131	8.9	1.2	0.2	<0.0004	8.6	0.0064	0.00122	0.36	*0.36*	1.5%
700.3, Inject $scCO_2$																
718.2	5.2 ± 0.2	4.3	0.02	135	0.45	134	9.1	1.1	0.5	<0.0004	9.0	0.0069	0.01281	13.35	**2406**	3.1%
742.3	5.2 ± 0.1	4.4	0.02	137	0.37	131	9.2	0.9	0.6	<0.0004	8.8	0.0033	0.01095	15.44	**2405**	1.3%
814.8	5.2 ± 0.1	4.4	0.02	136	0.39	135	8.9	0.9	0.6	<0.0004	9.3	0.0009	0.00741	15.34	**2406**	3.0%
1053.7	5.3 ± 0.1	4.4	0.02	137	0.28	136	10.7	1.0	0.6	<0.0004	8.7	0.0007	0.00640	14.29	**2404**	3.6%
1318.6	5.6 ± 0.1	4.7	0.02	137	0.30	134	10.3	1.1	0.5	<0.0004	8.2	0.0004	0.00525	17.76	**2405**	2.4%
1726.5	5.3 ± 0.1	4.4	0.02	125	0.19	129	10.6	1.8	0.7	<0.0001	7.5	0.0008	0.00424	19.24	**2414**	6.3%
Quench[d]	6.1 ± 0.3	6.3	0.03	126	0.92	130	9.7	2.5	0.7	<0.0001	7.3	0.0018	0.00861	6.83	--	5.2%
Uncertainty ± 1σ	--	--	0.02	10	0.04	4	0.4	0.3	0.1	--	0.5	0.0006	0.00007	±3.0%	--	--
Predicted Equilibrium Value[e], Pre-Injection	--	6.2	--	136	0.65	126	9.8	0.1	0.001	0.004	6.2	0.003	--	--	0.1	--
Predicted Equilibrium Value[e], Post-Injection	--	5.9	--	136	0.74	186	10.9	0.1	0.007	0.009	6.1	0.002	--	--	2380	--

From Lo Re et al. (2014)

Kinetic Mineral Dissolution Rates

$$r_m = A_m \cdot k_m \cdot \left\{1 - \left(\frac{Q_m}{K_m}\right)^{\mu}\right\}^{\eta}$$

where: m is mineral index, r_m is the dissolution/precipitation rate, A_m is the specific reactive surface area, k_m is the rate constants, K_m is the equilibrium constant for the mineral-water reaction, Q_m is ion activity product, μ, η are two positive numbers determined by experiment and usually taken equal to one.

Batch Simulations

- Mimic the batch experiments
- Primary minerals and initial volume fractions;
- Possible secondary minerals selection based on initial equilibrium batch modeling ;
- Kinetic properties at multiple mechanisms (neutral, acid, and base)
- Specific reactive surface area from BET measurements at laboratory;
- Thermodynamic database: EQ3/6 database;
- Simulation period: 2000 hours;
- CO_2 injection with a small amount for an hour around 670-700 hours.

Mineralogical Composition

Mineral	Chemical composition	Initial volume fraction of minerals				
		EXP-1	EXP-2	EXP-3	EXP-4	EXP-5
Primary:						
Quartz	SiO_2	0.3184	0.3189	0.3178	0.1805	0.1805
Oligoclase-uwy[a]	$Na_{0.77}Ca_{0.23}Al_{1.23}Si_{2.77}O_8$	0.3184	0.3189	0.3187	0.1805	0.1805
Albite	$NaAlSi_3O_8$	0.0805	0.0804	0.0806	0.0456	0.0456
K-Feldspar	$KAlSi_3O_8$	0.2472	0.2469	0.2474	0.1401	0.1401
Annite	$KFe_3AlSi_3O_{10}(OH)_2$	0.0145	0.0143	0.0145	0.0082	0.0084
Phlogopite	$KAlMg_3Si_3O_{10}(OH)_2$	0.0209	0.0206	0.0209	0.0119	0.0121
Epidote	$Ca_2Al_2(Fe^{3+},Al)(SiO_4)(Si_2O_7)O(OH)$	--	--	--	0.4331	0.4327
Porosity	-	0.9814	0.9815	0.9813	0.9877	0.9835
Calcite	$CaCO_3$	0.0	0.0	0.0	0.0	0.0
Magnesite	$MgCO_3$	0.0	0.0	0.0	0.0	0.0
Illite	$(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$	0.0	0.0	0.0	0.0	0.0
Smectite	$K_{0.04}Ca_{0.5}(Al_{2.8}Fe_{0.53}Mg_{0.7})(Si_{7.65}Al_{0.35})O_{20}(OH)_4$	0.0	0.0	0.0	0.0	0.0
Kaolinite	$Al_2Si_2O_5(OH)_4$	0.0	0.0	0.0	0.0	0.0
Chlorite	$Mg_{2.5}Fe_{2.5}Al_2Si_3O_{10}(OH)_8$	0.0	0.0	0.0	0.0	0.0
Muscovite	$KAl_3Si_3O_{10}(OH)_2$	0.0	0.0	0.0	0.0	0.0
Hematite	Fe_2O_3	0.0	0.0	0.0	0.0	0.0
Dolomite	$CaMg(CO_3)_2$	0.0	0.0	0.0	0.0	0.0
Ankerite	$CaMg_{0.3}Fe_{0.7}(CO_3)_2$	0.0	0.0	0.0	0.0	0.0
Dawsonite	$NaAlCO_3(OH)_2$	0.0	0.0	0.0	0.0	0.0
Siderite	$FeCO_3$	0.0	0.0	0.0	0.0	0.0

a) Oligoclase at specific ratio used for batch experiment by University of Wyoming.

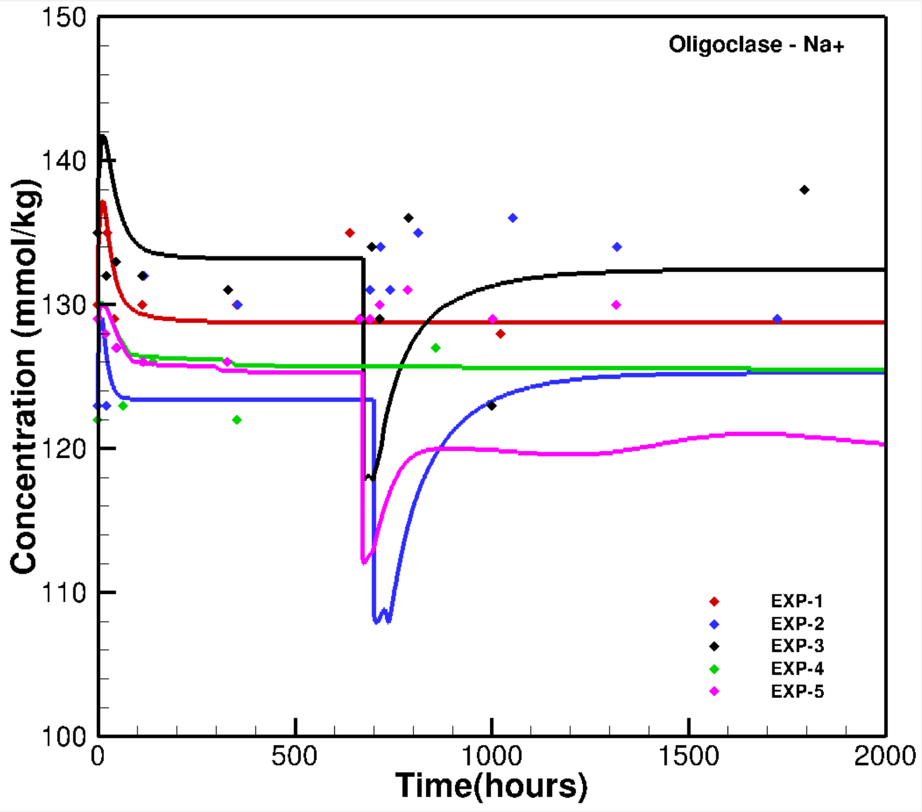
Kinetic Rate Parameters

Mineral	Neutral Mechanism		Acid Mechanism			Base mechanism		
	logk [a]	E_a [b]	logk [a]	E_a [b]	n [c]	logk [a]	E_a [b]	n [c]
Primary:								
Quartz	-13.99	87.7	-	-	-	-	-	-
Oligoclase	-11.84	69.8	-9.67	65.0	0.457	-	-	-
Albite	-12.56	69.8	-10.16	65.0	0.457	-15.6	71.0	-0.572
K-Feldspar	-12.41	38.0	-10.06	51.7	0.500	-21.2	94.1	-0.823
Annite [d]	-12.55	22.0	-9.84	22.0	0.525	-	-	-
Phlogopite	-12.40	29.0	-	-	-	-	-	-
Epidote	-11.99	70.7	-10.60	71.1	0.338	-17.33	79.1	-0.556
Chlorite	-12.52	88.0	-11.11	88.0	0.500	-	-	-
Calcite	-5.81	23.5	-0.30	14.4	1.000	-	-	-
Secondary:								
Calcite	-5.81	23.5	-0.30	14.4	1.000	-	-	-
Magnesite	-9.34	23.5	-6.38	14.4	1.000	-	-	-
Illite [e]	-13.55	22.0	-11.85	22.0	0.370	-14.55	22.0	-0.200
Smectite	-12.78	35.0	-10.98	23.6	0.340	-16.52	58.9	-0.400
Kaolinite	-13.16	22.2	-11.31	65.9	0.777	-17.05	17.9	-0.472
Chlorite	-12.52	88.0	-11.11	88.0	0.500	-	-	-
Muscovite	-13.55	22.0	-11.85	22.0	0.370	-14.55	22.0	-0.220
Hematite	-14.60	66.2	-9.39	66.2	1.000	-	-	-
Dolomite	-7.53	52.2	-3.19	36.1	0.500	-5.11	34.8	0.500
Ankerite [f]	-7.53	52.2	-3.19	36.1	0.500	-5.11	34.8	0.500
Dawsonite	-7.00	62.8	-	-	-	-	-	-
Siderite	-8.90	62.8	-3.19	36.1	0.500	-	-	-

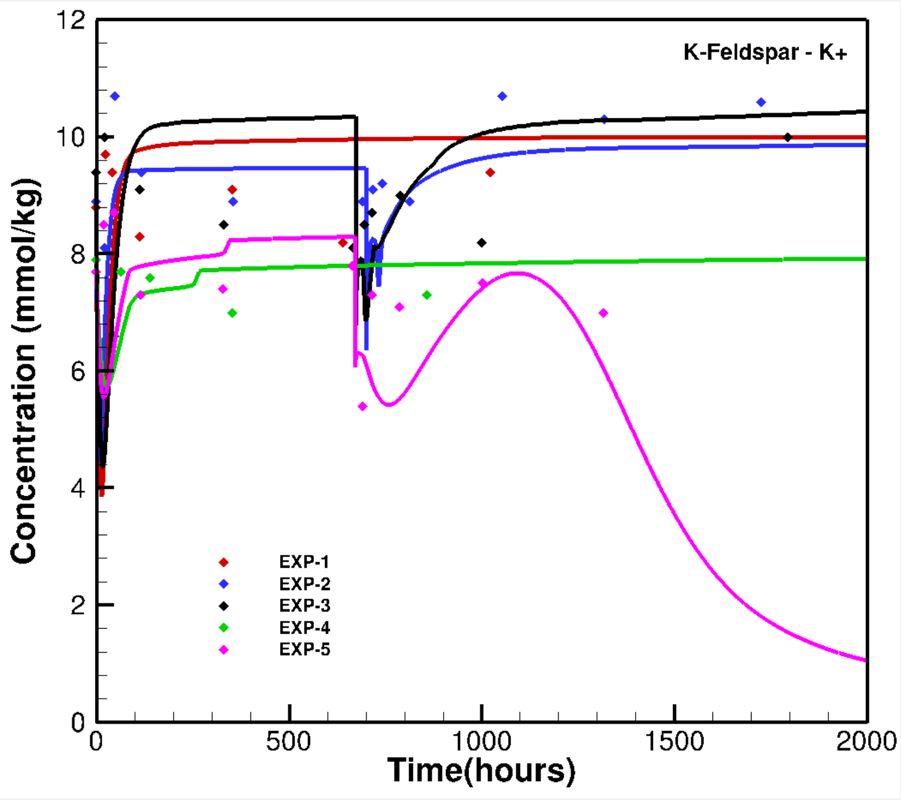
Note: Kinetic rate parameters from Palandri and Kharaka (2004);
a) logk: kinetic rate constant k at 25 ^oC ($mol/m^2/s$);
b) E_a: activation energy (KJ/mol);
c) n: power term with respect to H^+;
d) set to Biotite; e) set to Muscovite; f) set to Dolomite

Calibration

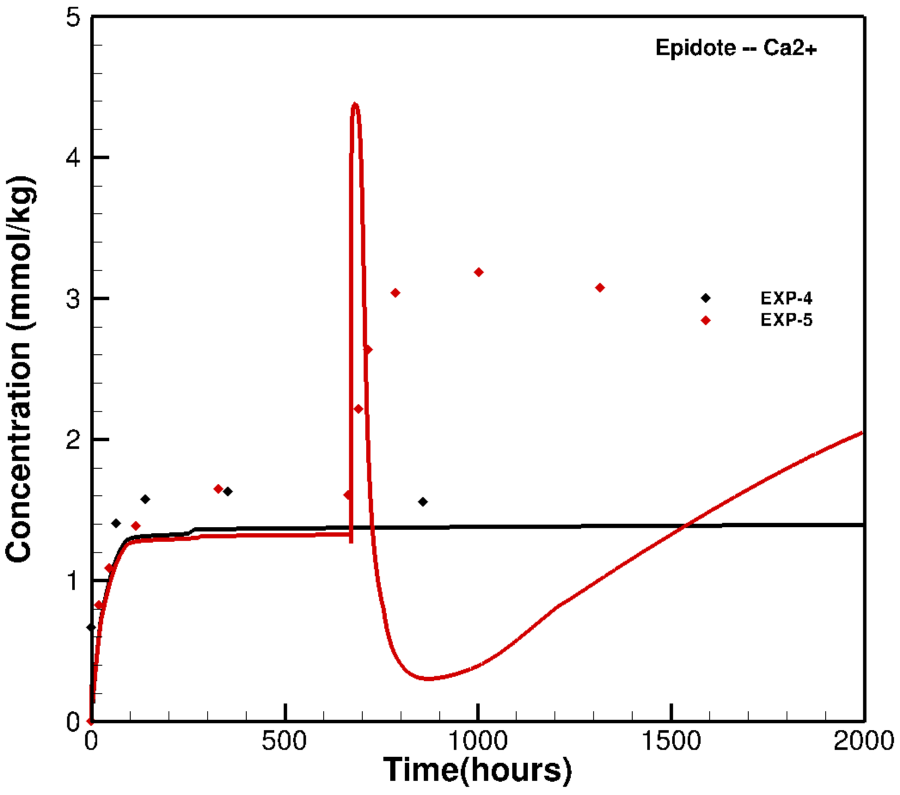
- Parameters:
  - kinetic rate constant
  - reactive surface area
- Minerals:
  - Albite and Oligoclase against measured Na^+ concentration
  - K-feldspar against measured K^+ concentration
  - Epidote against measured Ca^{2+} concentration
- Methods:
  - Parameter estimation tool (iTOUGH2-PEST) coupled with TOUGHREACT model



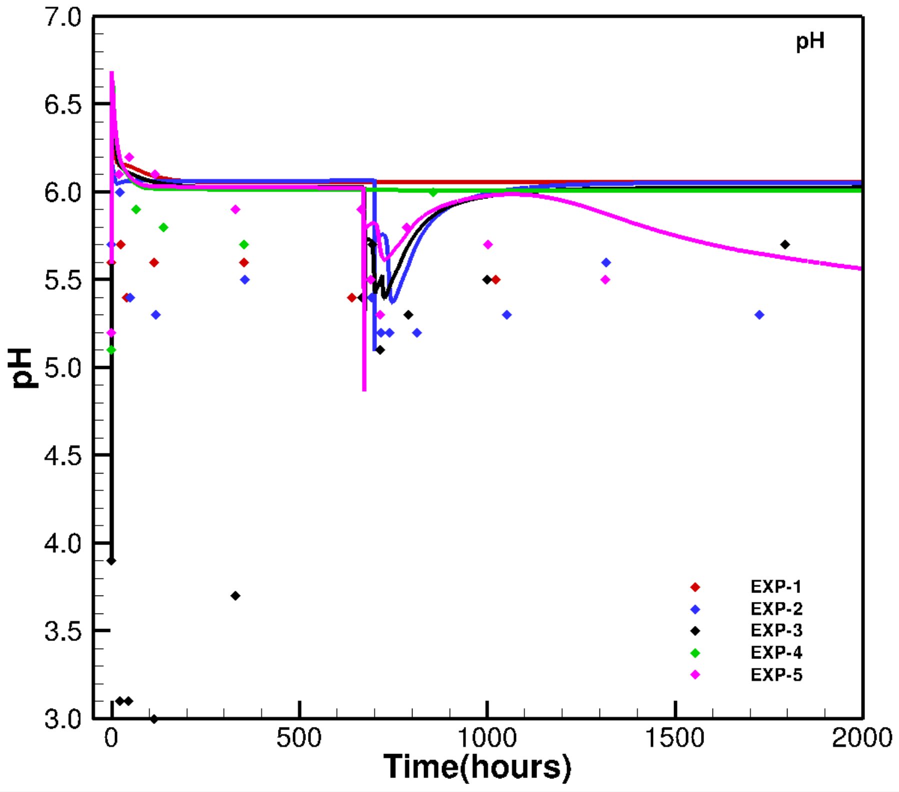
Measured and simulated Na+ concentration over time associated with calibration.



Measured and simulated K+ concentration over time associated with calibration.



Measured and simulated Ca2+ concentration over time associated with calibration.



Measured and simulated pH values over time as a result of calibration.

Calibrated kinetic rate constants of minerals Albite, Oliogclase, K-Feldspar, and Epidote for EXP-1 to EXP-5.

Minerals	K_{25} (mol/m^2/s)	Calibrated K_{25} (mol/m^2/s)				
		EXP-1	EXP-2	EXP-3	EXP-4	EXP-5
Oligoclase	0.145e-12	0.100e-12	0.100e-12	0.100e-12	0.100e-12	0.100e-12
Albite	0.275e-12	0.300e-12	0.300e-12	0.300e-12	0.300e-12	0.300e-12
K-Feldspar	0.389e-12	0.700e-10	0.300e-10	0.200e-10	0.220e-11	0.200e-11
Epidote	0.102e-11	--	--	--	0.100e-11	0.260e-10

Calibrated reactive surface area of minerals Albite, Oliogclase, K-Feldspar, and Epidote for EXP-1 to EXP-5.

Minerals	Measured Surface area (cm^2/g)	Calibrated surface area (cm^2/g)				
		EXP-1	EXP-2	EXP-3	EXP-4	EXP-5
Oligoclase	6,303	6,000	6,000	6,000	6,000	5,670
Albite	9,270 (EXP-2, 4, 5) 4,408 (EXP-1,3)	4,500	9,300	4,500	9,300	9,300
K-Feldspar	9,270 (EXP-2, 4, 5) 4,408 (EXP-1,3)	10,000	50,000	9,000	14,000	22,000
Epidote	6,327	--	--	--	6,400	5,600

Summary

- Overall, the simulated major cation concentrations for the experiments without CO_2 injection have better agreement with measured values than simulations of experiments with CO_2 injection.
- The calibrated reactive surface area are several times larger than the BET measured values for K-feldspar. A longer reaction period may be necessary for batch experiments to provide more effective calibration of mineral reactive surface areas and kinetic parameters.
- Simulated pH values for calibrations generally exhibit good agreement with measured values.
- Calibrated kinetic parameters can be used for related geochemical simulations in EGS reservoirs at elevated temperature and pressure.

Questions?